

Preparation, characterization and study of morphology of activated carbon fibers

Preparación, caracterización y estudio morfológico de fibras de carbón activado

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Abstract

Using kenaf as starting material, a study about the preparation and characterization of activated carbon fibers (ACFs) from long fibers was carried out. The carbonization products of kenaf fibers and ACFs were texturally characterized by N₂ adsorption at -196 °C, mercury porosimetry, and scanning electron microscopy.

The activation of the raw material of Kenaf by its carbonization at 400 °C for 0.5 h in a N₂ atmosphere increase the porosity of the samples, particularly the activation at 700 °C with carbon dioxide. It should be noted the porous development shown by the scanning electron micrographs of samples FBC4A72 and FBC4A74. It is observed that the variation of treatment time from 2 to 4 hours leads to an important development of the porous structure in samples FBC4A74, which is probably a consequence of an interconnection between pores. These results open a wide field of applications of these fibers.

Resumen

Utilizando fibras de kenaf larga, se ha llevado a cabo la preparación, caracterización y estudio morfológico de las fibras de carbón activado (ACFs). La caracterización era realizada mediante las isothermas de adsorción de N₂ a -196 °C, porosimetría de Hg y microscopía electrónica de barrido. La activación a 700 °C con CO₂ durante 2h (FBC4A72) y 4 h (FBC4A74) de la muestra carbonizada a 400 °C durante 0.5 h en N₂ (FBC4), mostraban un incremento en el tamaño del poro, como se observa en las microscopías electrónica de barrido. Esto es probablemente debido a la interconexión de los poros como consecuencia del incremento del tiempo de tratamiento de 2 a 4h. Estos resultados abren un amplio campo de aplicación para las fibras de kenaf.

1. Introduction

Activated carbon fibers (ACFs) constitute a particular type of activated carbon, the morphology of ACF being fibrous in nature. ACFs present certain specific advantages in comparison to other activated carbons. Because of their large surface area, porous character and high adsorption/desorption rate they are widely used as adsorbents in numerous applications [1].

A potential precursor of ACFs is Kenaf, possesses two types of fibers: the bark and the woody nuclei, which represent about 30 % and 70 % of the crop, respectively. So far, these fibers have been mostly used to obtain textile and paper products, which compete strongly with wood and synthetic fibers. As a result, the possibility of using natural fibers in other

applications has not been developed extensively [2,3]. The main objective of the present work was to carry out the preparation and characterization of ACFs obtained from Kenaf.

2. Experimental

2.1. Starting material

Kenaf (2-3 cm diameter trunks) supplied by the Junta de Extremadura (Spain) was used. The received trunks were air-dried, that easily enables isolate, either manually or mechanically, the long fibers (outer part) from the short fibers (inner part) and then the longer fibers one by one. After this step, only the longer fibers (KFs, hereafter) were selected for subsequent studies.

2.2. Chemical analyses of KFs

The cellulose, hemicellulose and lignin content were determined by the Tappi method [4,5].

Data of the proximate analysis of KFs (Table 1) were obtained using a thermogravimetric method [6] and elemental analysis was performed on a dry basis using a model CE440 Elemental Analyzer (Table 1).

2.3. Carbonization of KFs

The carbonization of KFs was developed in a tubular furnace consisting of a Termolab with Eurotherm 904 temperature controllers and a 1 meter-tubular ceramic inserted. About 1.5 g of KFs was placed in a 10 cm stainless steel boat with perforated ends to facilitate gas flow. The boat was positioned in the centre of the constant temperature zone. The carbonization of the fibres was carried out at 300 and 400° C in N₂ atmosphere (flow rate of 85 mL min⁻¹). The heating rate from room temperature to the maximum heat temperature (MHTT) was 5 °C min⁻¹. The heating time at MHTT was 0.5 and 1 h. The notations used for the carbonized fibers (CFs) were FBCT fibers carbonized at 300-400°C for 0.5 h and FBCT1 carbonized fibers carbonized at 300-400°C for 1 h; T will be equal to 3 or 4 as a function of the temperature (3 in the case of a temperature of 300 °C and 4 in the case of 400 °C).

2.4. Preparation of ACFs

Using the same calefaction system used in the carbonization treatments, the fiber carbonized at 400 °C for 0.5 h (FBCT) was used as intermediate product and was activated at 500, 600 and 700° C in a carbon dioxide atmosphere (flow rate = 85 mL min⁻¹). The heating rate was 5 °C min⁻¹, and the soaking time was 2 and 4 h. The notations used was FBC4ATt, where FBC4 represents fibers carbonized at 400°C for 0.5h, A, represents the activation with carbon dioxide, T is

the activation temperature (500-700°C), and t is the activation time (2 or 4 h).

2.5. Characterization

The characterization of CFs and ACFs was carried out by physical adsorption of N_2 at -196°C. The adsorption isotherms were measured using a Quantachrome apparatus (Autosorb 1). From such isotherms, the specific surface area (S_{BET}) was calculated by applying the BET equation [7]. The micropore volume (W_0) was obtained using the Dubinin-Radushkevich equation [8]. Also, the micropore volume (V_{mi}) was derived by simply reading the volume adsorbed (V_{ad}) at $P/P^0=0.1$ and the mesopore volume (V_{me}) by subtraction of V_{mi} from V_{ad} at $P/P^0=0.95$; W_0 , V_{mi} , and V_{me} being expressed as liquid volumes. Finally, the pore size distribution in the micropore and mesopore ranges was obtained using the Density Functional Theory (DFT) [9] and BJH methods [10]. On the other hand, information about the meso- and macroporous structures of selected ACFs was obtained by mercury porosimetry, using a Micromeritics porosimeter in the range of 0.10 – 441 MPa. The sample morphology was observed by scanning electron microscopy (SEM) using a S-3600N microscope (Hitachi, Japan).

3. Results and discussion

3.1. Chemical composition of KFs

Numerous studies performed by other authors (Stone J, Scallan A, Duchesne, and Daniel G.) show the important role that plays the contents of lignin and hemicellulose within the Kenaf in the development of its porous structure. Thus, it is observed that the reduction in lignin and hemicellulose content is directly related to the development of the porous structure [11,12]. Lignin is a natural adhesive that contains aromatic rings. These rings does not contribute to the porous development at low temperatures, nevertheless the higher temperatures favor the porous development.

The content in cellulose (69.8%), hemicellulose (12.6%) and lignin (17.6%) seem to indicate that the Kenaf fiber can be an excellent precursor in the preparation of ACFs, not finding any work related to this aspect in bibliography [13-15].

Results obtained in the proximate analysis of KFs (Table 1) indicate that this material is largely composed of volatile matter and has a low inorganic fraction. Despite the low value of fixed C, we find possible the preparation of activated carbon fibers. The special characteristics of the fibers obtained, tubular structures, would allow set functional groups and improve their absorbent properties.

Table 1. Proximate analyses and elemental analysis of Kenaf fibers.

Tabla 1. Análisis aproximado y elemental de fibras de Kenaf.

| Proximate analysis, wt. % | | Elemental analysis, wt. % | |
|---------------------------|------|---------------------------|------|
| Moisture | 10.3 | C | 55.3 |
| Volatile matter | 74.0 | O | 39.3 |
| Ashes ^a | 2.7 | N | 0.3 |
| Fixed carbon | 13.0 | H | 5.1 |

^a Average value of triplicate analyses.

The elemental analysis (Table 1) seems to indicate that the high content of volatile matter (74%) could be related to the transformation of an important part of the carbon present in the raw material (55.3%) in volatile, which would justify the value of fixed carbon obtained.

3.2. Textural characterization of carbonized fibers

Figure 1 shows the N_2 adsorption isotherms determined for the carbonized fibers. They reveal that the extent of N_2 adsorption is lower in FBC31 and FBC41 than FBC3 and FBC4, and also that the larger adsorption capacity correspond to FBC4.

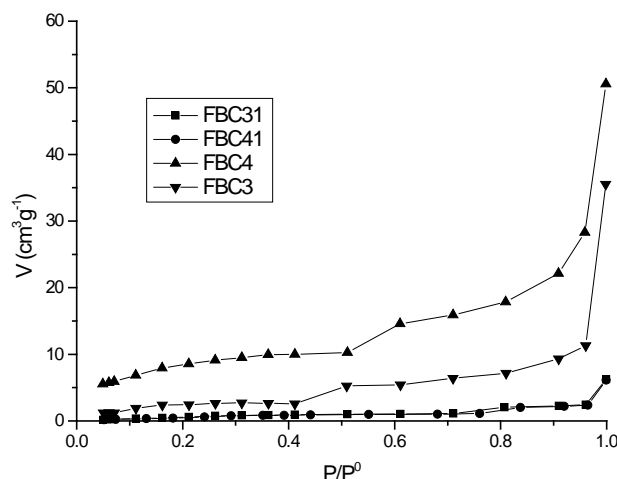


Figure 1. Adsorption isotherms of N_2 at -196°C of the carbonized fibers.

Figura 1. Isotermas de adsorción de N_2 a -196°C de fibras carbonizadas.

The shape of the isotherms resembles the type IV isotherms of the well-known BDDT classification system. Accordingly, the carbonized fibers are principally mesoporous carbons.

The textural parameters corresponding to the carbonized fibers are gathered in the Table 2.

S_{BET} ranges between 3 $m^2 g^{-1}$ for FBC31 and FBC41 and 29 $m^2 g^{-1}$ for FBC4. The microporous volume, both V_{mi} and V_{DR} , is very low in all samples. The largest value of V_{mi} (0.011 $cm^3 g^{-1}$) corresponds to

Table 2. Textural parameters of the carbonized fibers.

Tabla 2. Parámetros texturales de las fibras carbonizadas

| Sample | S_{BET} ($m^2 g^{-1}$) | W_0 ($cm^3 g^{-1}$) | V_{mi} ($cm^3 g^{-1}$) | V_{me} ($cm^3 g^{-1}$) | V_{me-p} ($cm^3 g^{-1}$) | V_{ma-p} ($cm^3 g^{-1}$) | APS (Å) |
|--------|-------------------------------|----------------------------|-------------------------------|-------------------------------|---------------------------------|---------------------------------|------------|
| FBC3 | 8 | 0.005 | 0.003 | 0.015 | 0.010 | 0.021 | 8.57 |
| FBC4 | 29 | 0.016 | 0.011 | 0.030 | 0.031 | 0.034 | 6.85 |
| FBC31 | 3 | 0.001 | 0.0001 | 0.007 | 0.009 | 0.017 | 10.48 |
| FBC41 | 3 | 0.001 | 0.0001 | 0.009 | 0.010 | 0.028 | 10.49 |

FBC4. In contrast, V_{me} is as high as $0.030 \text{ cm}^3 \text{ g}^{-1}$ for FBC4.

From DFT plots obtained for the carbonized fibers (Fig. 2a) it is concluded that the pore size distribution is bimodal for FBC3 and FBC4. Notice that the pore size distribution in the regions of micropore and narrower mesopores is much wider in FBC4 than in FBC3. Furthermore, the larger mesopores present in these products are wider in FBC4. Thus, the more prominent peaks are located at 19.5 and 37.4 Å for FBC3 and at 17.5 and 46.2 Å for FBC4. From these results it becomes clear that the increase in the carbonization temperature provided that the heating time is short, gives rise to the creation and widening of pores. As far as the DTF plots for FBC3 and FBC4, they only display a single peak at close values of the pore width, which is centred between 25 and 30 Å. These results suggest that when the carbonization of Kenaf fibers at 300 and 400 °C is carried out for 1 h instead of 0.5 h, the widest mesopores disappear from the resultant products as a result of the increased devolatilization of the material and narrow mesopores are created, perhaps because of the widening of micropores.

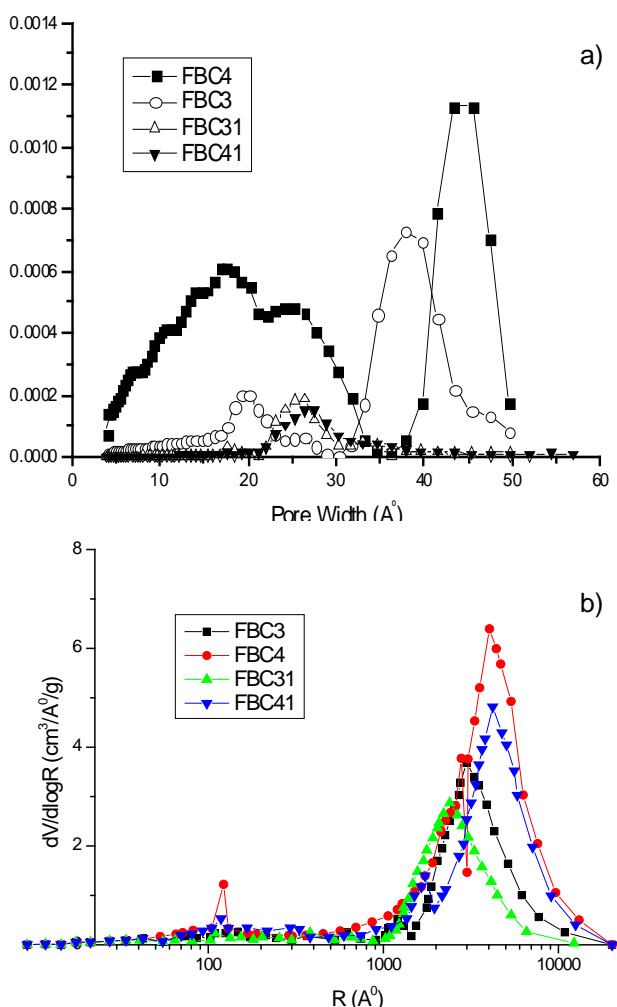


Figure 2. (a) DFT for the carbonized fibers, (b) Mercury porosimetry of the carbonized fibers

Figura 2. (a) DFT para fibras carbonizadas, (b) Porosimetría de mercurio de fibras carbonizadas

Figure 2b shows the pore size of carbonized fibers determined by mercury porosimetry. This distribution shows a peak at 130 Å and a small mercury intrusion in the mesopore region for the samples.

3.3. Textural characterization of activated carbon fibers

The N_2 adsorption isotherm at 77 K measured in the samples are shown in Figure 3. Isotherms are type IV according to the classification of BDDT. This figure shows the influence of two parameters: activation temperature (500-700 °C) and time of treatment (2 y 4h).

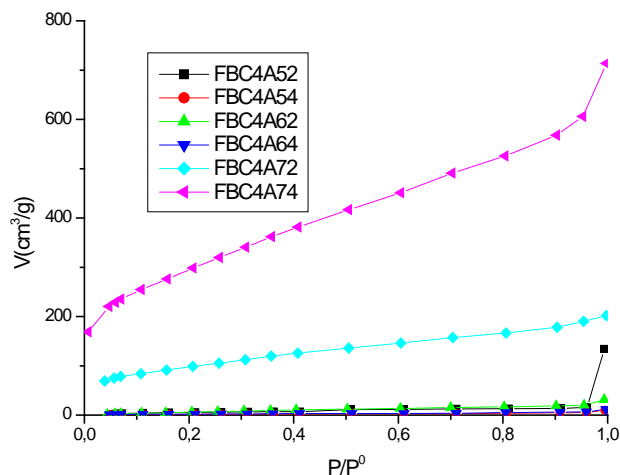


Figure 3. Adsorption isotherms of N_2 at -196°C of the activated carbon fibers.

Figura 3. Isoterma de adsorción de N_2 at -196°C de fibras de carbón activado.

On the one hand, it is observed that the isotherms obtained in the temperature range of 500-600° C and after 2h of constant treatment are very close to the x-axis, which indicates a low development of the specific surface ($21 \text{ m}^2 \text{ g}^{-1}$ and $33 \text{ m}^2 \text{ g}^{-1}$ respectively) Table 3. At temperatures of 700° C this parameters are remarkably increased ($341 \text{ m}^2 \text{ g}^{-1}$ in sample FBC4A72). However heat treatments for 4 h lead to a similar behavior to the previously observed with low values of specific surface in the range of 500-600° C and very high values after the treatment at 700° C (FBC4A74, $1031 \text{ m}^2 \text{ g}^{-1}$). These results are better than the previously found for similar ACFs in bibliography [16, 17], although in the present study lower temperatures have been used in the activation. Thus, for example, Gaur et al. [16] prepared ACFs by physical activation at temperatures of 800–1000° C. The maximum value of S_{BET} obtained at these temperatures was of $928 \text{ m}^2 \text{ g}^{-1}$. Using similar temperatures (800-1000° C) Ko et al. [17] prepared fibers of the coal obtaining maximum S_{BET} values of $161 \text{ m}^2 \text{ g}^{-1}$. This behavior can be attributed to the own structure of Kenaf consisting of layers and to their contents in cellulose, lignin and hemicellulose. The values of S_{BET} obtained for the samples treated at 700 °C during 2 and 4 h are quite similar to the values obtained by other authors using diverse fibers [18,20].

If we compared the obtained textural parameters of porosity with other values obtained for other fibers rich in cellulose such as rayon [18] ($V_{mi} = 0.68 \text{ cm}^3/\text{g}$, $V_{me} = 0.32 \text{ cm}^3/\text{g}$), we found high values for fibers obtained from Kenaf ($V_{mi} = 0.594 \text{ cm}^3/\text{g}$, $V_{me} = 0.544 \text{ cm}^3/\text{g}$). The good behavior of both fibers can obey to the composition with raw materials rich in cellulose. Furthermore, it is important to highlight that the porous development of this material is obtained when it works at low temperature, 700° C. This fact

Table 3. Textural parameters of the activated carbon fibers.

Tabla 3. Parámetros texturales de fibras de carbón activado.

| Sample | S_{BET} ($\text{m}^2 \text{g}^{-1}$) | W_0 ($\text{cm}^3 \text{g}^{-1}$) | V_{mi} ($\text{cm}^3 \text{g}^{-1}$) | V_{me} ($\text{cm}^3 \text{g}^{-1}$) | $V_{\text{me-p}}$ ($\text{cm}^3 \text{g}^{-1}$) | $V_{\text{ma-p}}$ ($\text{cm}^3 \text{g}^{-1}$) | APS (\AA) |
|---------|--|--|--|--|--|--|-------------------------|
| FBC4A52 | 21 | 0.012 | 0.007 | 0.018 | 0.020 | 0.036 | 9.36 |
| FBC4A54 | 7 | 0.004 | 0.002 | 0.006 | 0.006 | 0.040 | 8.98 |
| FBC4A62 | 33 | 0.016 | 0.016 | 0.026 | 0.024 | 0.048 | 11.00 |
| FBC4A64 | 8 | 0.005 | 0.003 | 0.080 | 0.092 | 0.060 | 8.78 |
| FBC4A72 | 341 | 0.181 | 0.130 | 0.164 | 0.154 | 0.021 | 5.83 |
| FBC4A74 | 1031 | 0.551 | 0.594 | 0.544 | 0.501 | 0.018 | 5.96 |

is reviewed by other authors in materials with an elevated content of lignin ($V_{\text{mi}} = 0.53 \text{ cm}^3/\text{g}$) [19].

The porosity values ($V_{\text{mi}} = 0.594 \text{ cm}^3/\text{g}$, $V_{\text{me}} = 0.544 \text{ cm}^3/\text{g}$) obtained for Kenaf at 700°C and variable times of treatment are superior to the values found in bibliography [18-20]. The effect of the time affects in a different way and in a larger magnitude at 700°C .

On the other hand, the size distributions in micro, meso and macropores shown in Figures 4 y 5 and present two different behaviors.

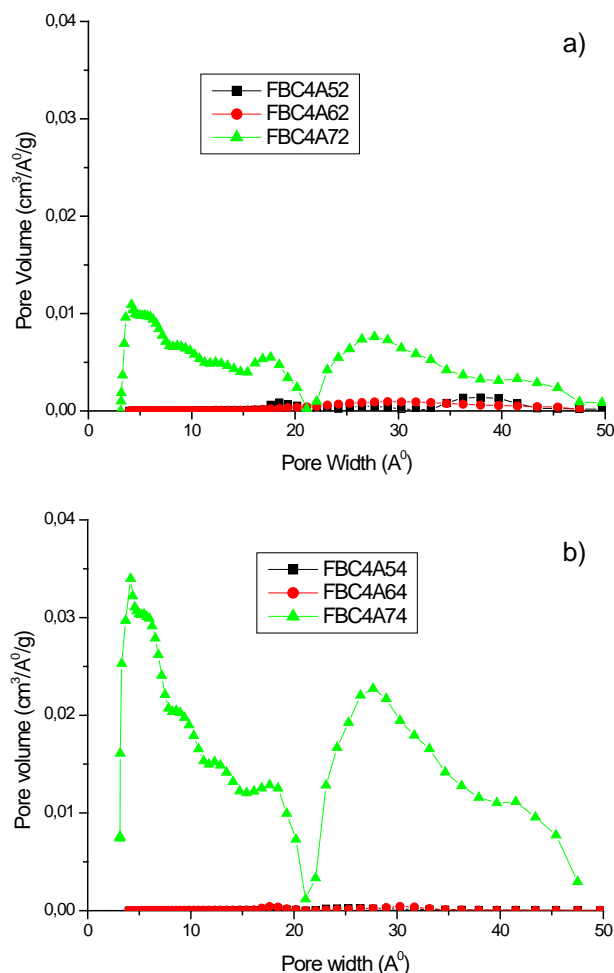


Figure 4. (a) DFT for the activated carbon fibers (2h) and (b) (4h).
Figura 4. (a) DFT de fibras de carbón activado (2h) and (b) (4h).

The value obtained in the range temperature of $500\text{--}600^\circ \text{C}$ with a time of constant treatment of 2h, is very close to the x-axis, which indicates a low development of micropores and mesopores. At temperatures of 700°C (Fig. 4a) these parameters are remarkably increased (4.17 \AA and 28.4 \AA) in sample FBC4A72. However, when heat treatments are maintained for

4 h, a similar behavior is observed, but with slightly lower values than in the previous case.

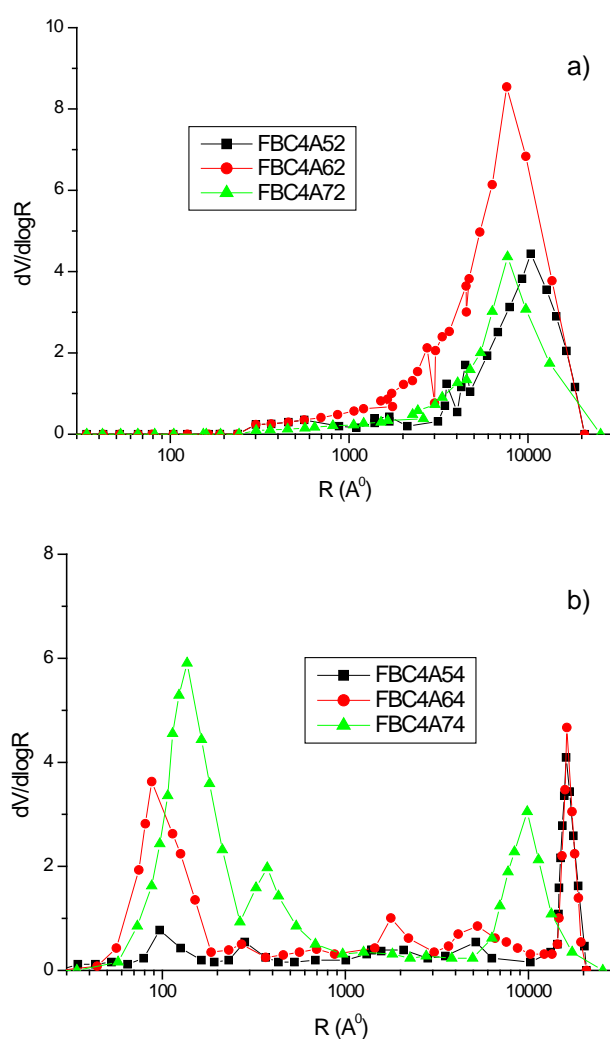


Figure 5. Mercury porosimetry of the activated carbon fibers a) 2h and b) 4h

Figura 5. Porosimetría de mercurio de fibras de carbón activado (a) 2h y (b) 4h

The results of the mercury porosimetry shown in Figs. 5a and 5b presents two noticeable behaviors depending on the studied variables (temperature and time). Thus, when the temperature of treatment is analyzed, a low development of porosity is observed but it is slightly superior for the samples treated at temperatures under 700°C , especially in the band of macropores. When we study the effect of the treatment time, it is observed that low porous development (in the strip of the mesopores) corresponds to times of 2 h, in the strip of the mesopores; however, greater porous development corresponds to times of 4 h,

pores being distributed in the zone of mesopores and macropores.

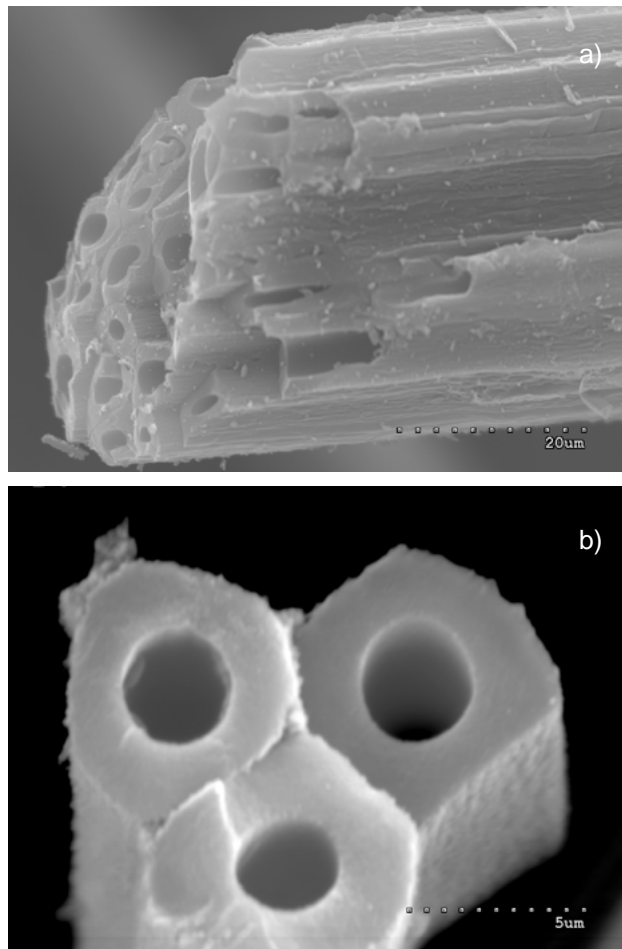


Figure 6. SEM micrograph of sample (a) FBC4A72 and (b) FBC4A74.

Figura 6. Micrografía SEM de las muestras (a) FBC4A72 and (b) FBC4A74.

Finally, with the aim of corroborating the tendencies of porous development observed in the previous sections, the morphologic evolution of pores throughout all the prepared series was studied. Special attention was focused on the samples prepared at 700 °C (Fig.6a and Fig.6b). Thus, by comparing micrographs of FBC4A72 (Fig.6a) with the FBC4A74 (Fig.6b), a marked porous development was observed in the samples. A subsequent comparison of these samples with respect to the treatment time (activation at 700 °C and 2h and 4h of treatment) (Fig. 6a and 6b) reflects a homogenous and uniform distribution of macropores and a greater size of pore of the sample FBC4A74. Probably, this effect obeys to the interconnection of pores and to the treatment time. These results open a wide field of applications for these types of fibers.

4. Conclusions

The activation of the raw material of Kenaf by its carbonization at 400 °C during 0.5 h in N₂ atmosphere develops the porosity of the samples. The activation at 700 °C under carbon dioxide atmosphere, both during 2 h and during 4 h, provokes greater values of textural parameters S_{BET} , W_0 , V_m and V_{me} than the provoked to the activation at inferior temperatures (500 and 600 °C). Furthermore, results obtained at an activated temperature of 700 °C were similar (in the case of S_{BET}) or even superior (in the case of V_m

and V_{me}) to the results obtained by other authors that used diverse fibers. These results imply a wide field of applications for these fibers.

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